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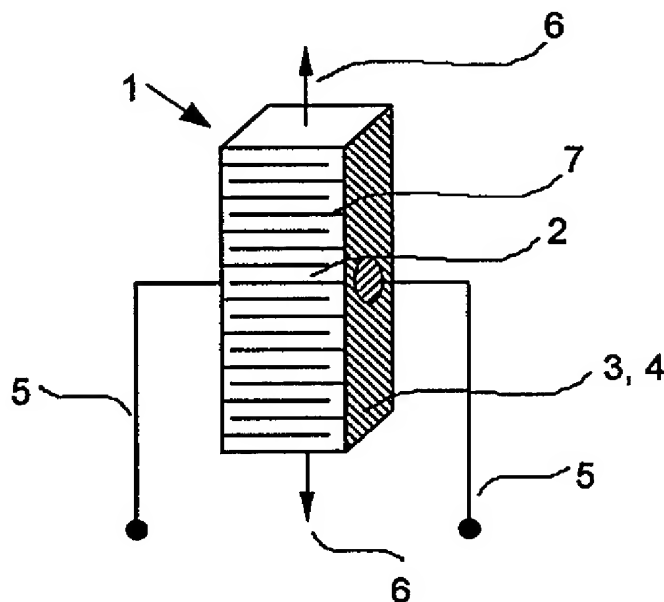
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(54) Title: INTERNAL ELECTRODE MATERIAL FOR PIEZOCERAMIC MULTILAYER ACTUATORS



(57) Abstract: A piezoceramic multilayer actuator comprising a low-sintering piezoceramic composition based on modified lead zirconium titanate and an inner metallization electrode (2) composition comprising silver and platinum.

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For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

**WO 01/93345 A1**



## INTERNAL ELECTRODE MATERIAL FOR PIEZOCERAMIC MULTILAYER ACTUATORS

### FIELD OF THE INVENTION

This invention relates to a silver platinum composition for use as an internal electrode material for a piezoceramic multilayer actuator.

### BACKGROUND

Piezoceramic multilayer actuators (PMA) as shown in Figure 1 consists of stacked thin layers of piezoelectrically active material 7, for example, lead-zirconate-titanate (PZT), with conductive internal electrodes 2 placed in between them, which are alternately directed toward the actuator surface. External electrodes 3,4 interconnect these internal electrodes. Thus, the internal electrodes are electrically connected in parallel and combined into two groups that represent the two connecting poles of the actuator. If one applies an electrical voltage to the connecting poles, this voltage is transferred in parallel to all internal electrodes and produces an electrical field in all layers of the active material, which is thereby mechanically deformed. The sum of all of these mechanical deformations is available at the end faces of the actuator as a usable expansion 6 and/or as a force.

According to the state of the art, piezoceramic multilayer actuators are designed as monoliths, that is the active material, in the form of a organic containing, green (not fired) film, is provided with internal electrodes by means of silk-screen printing, pressed into actuator stacks, pyrolyzed and then sintered, whereby the monolithic actuator is produced.

As shown in Figure 1, a base metallization 3 is applied to the actuator stack 1 in the region of the exiting internal electrodes 2, by galvanic processes or by screen-printing a metal composition (paste). The base metallization is thickened by applying a metallic material 4 by soldering on a structured sheet metal or a wire mesh. The electrical connecting lead 5 is soldered to this thickened layer.

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Figure 1 shows a general configuration of a PMA. Figure 2 shows further details. The structure and the production of such actuators and external electrodes is described in detail in DE 33 30538 A1, DE 40 36 287 C2, US 5,281,885, US 4,845,399, US 5,406,164 and JP 07-226541 A and are incorporated herein as reference.

The basic requirement of the method of operation is that the metallic internal electrode can be sintered together with the piezoceramic. Sintering at temperatures of 1100-1200°C in a normal air atmosphere is necessary for piezoceramics manufacture according to the state of the art. Therefore, it is necessary to select a material for the internal electrode that does not oxidize under sintering conditions and does not change in volume or react with the ceramic which would cause a negative effect on its properties.

Alloys or mixtures of silver and palladium are usually used for the internal electrode. Pd is necessary in order to raise the melting point (liquidus point) of the internal electrode. A usual fraction of 30 weight-percent Pd leads to a melting point of 1130°C, which is sufficient for current actuator production. In addition, the Pd fraction causes suppression of the diffusion of Ag into the ceramic during sintering. Although the diffusion of Ag cannot be completely prevented, the negative influence on the piezoelectric characteristics can be minimized by the formulation of the ceramic as found in EP 0 894 341 B1.

However, the use of silver palladium, usually AgPd 70/30, as the internal electrode involves many negative aspects, particularly in the mass production of actuators. Palladium is rare and expensive and its price is speculative. Palladium oxidizes at temperatures near 400°C and thereby changes its volume substantially. At temperatures near 700°C, Pd is again reduced. This effect cannot be completely avoided. However, actuators are mechanically very sensitive in the corresponding temperature range. The change in volume can therefore lead to a loss of the bonding of the internal electrode to the ceramic, to a low fracture resistance or to delamination of the actuator.

Formulations for solving these problems by reducing the sintering temperature of the piezoceramic and the simultaneous minimization of the Pd-fraction of the internal electrodes have not been successful to date because the diffusion of the silver into the ceramic then comes to the fore, and this affects its characteristics negatively.

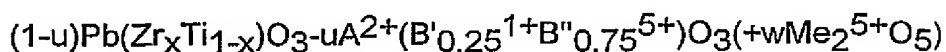
- 5 Therefore, the composition of the present invention replaces the palladium with platinum for use in compositions for internal electrodes.

This substitution leads to the following advantages. Platinum does not oxidize, thus does not change its volume and does not react with the ceramic. Actuators with such Ag/Pt electrodes are substantially more resistant against fracture than AgPd internal electrodes. Internal electrodes containing platinum can be produced in a manner such that they obtain a lattice structure on sintering which leads to an increased fracture resistance. Platinum is substantially more effective as an inhibitor of silver diffusion than Pd which reduces the amount of Pt needed than in comparable AgPd internal electrodes.

- 15 The only disadvantage of using platinum is that it does not increase the melting temperature of the internal electrode alloy as much as palladium. So, ceramics presently used in the industry cannot be used with Ag/Pt since their sintering temperature is 1100-1200°C in a normal air atmosphere. If AgPt is to be used in the compositions for internal electrodes, then the sintering temperature of the piezoceramic should be in the range of 875-1000°C and all ranges contained therein. A ceramic which sinters within this range is described in DE 198 40 488 A1 which is a lead zirconium titanate piezoelectric ceramic material. The method of using this ceramic with a Ag/Pt composition is discussed herein.

### SUMMARY OF THE INVENTION

- 25 The present invention relates to a piezoceramic multilayer actuator comprising a low-sintering piezoceramic material being expressed by the following general formulas,



wherein

20 Figure 1 is a schematic representing a piezoceramic multilayer actuator.

Figure 2 is a schematic representing a cross section of a piezoceramic multilayer actuator.

# BRIEF DESCRIPTION OF THE DRAWINGS

and an inner metallization comprising silver and platinum.

15  $x = 0.40 \dots 0.55$   
 $u = 0 \dots 0.10$   
 $u, v = 0 \dots 0.05$

and x, y, u, and v have the following meaning:  
 $B^{5+}$ , for a 5-valent metal ion from the series Nb, Ta, or Sb, preferably for Nb;  
 $A^{1+}$  stands for alkali metal ions, preferably for  $Na^+$  and/or  $K^+$ ;  
 wherein

10  $(1-u-v)Pb(Zr_xTi_{1-x})O_3-uA^{1+}B^{5+}O_3-v(Sr_{1-y}Ba_y)_2Nb_2O_7$

or

5  $x = 0.40 \dots 0.55$   
 $u = 0 \dots 0.10$   
 $(w = 0 \dots 1 \text{ wt. \%})$

and x, u, and w have the following meaning:  
 $B''$  and Me for a 5-valent metal from the series Nb, Ta, or Sb, preferably Nb  
 $B'$  stands for alkali metal, preferably for Na and/or K;  
 $A^{2+}$  stands for alkaline earth metal ions, preferably for  $SR^{2+}$  and/or  $Ba^{2+}$ ;

## DETAILED DESCRIPTION OF THE INVENTION

### Internal Electrode Composition

The compositions, which form the internal electrode of a PMA, are comprised of finely divided particles of metal and/or ceramic (referred to as "solids") dispersed with polymers in organic solvent (referred to as "organic medium"). Such compositions are generally called "thick film compositions" which are well known to those skilled in the art of electronic materials. Finely divided silver and platinum powders, in spherical and/or flake form, within the range of 0.5 micron to 20 micron, with a mixing ratio in the range of 70/30 weight percent to 98/2 weight percent and all ranges contained therein are used as the metal powders according to this invention. Preferably, a 90/10 AgPt mixture is used. With addition of ceramic powder, which preferably has an average grain size of the magnitude of the layer thickness of the interior metallization, the amount of metal powder can be reduced to an electrically necessary minimum. This minimum is determined by the electrical resistance of the internal electrode and the maximum allowable resistive energy dissipation. It is preferred to match the ceramic powder to the piezoelectrically active material used in the PMA. The most preferred ceramic powder is lead-zirconate-titanate powder.

The organic medium is conventional in the art and is typically a solution of resin(s) or polymer(s) in solvent(s). Any essentially inert liquid may be used as the organic medium. The organic medium must be one in which the solids are dispersible with an adequate degree of stability. The rheological properties of the medium must be such that they lend good application properties to the composition. Such properties include: dispersion of solids with an adequate degree of stability, good application of composition, appropriate viscosity, thixotropic, appropriate wettability of the substrate and the solids, a good drying rate, good firing properties, and a dried film strength sufficient to withstand rough handling. Examples include: aliphatic alcohols, esters of such alcohols, for example, acetates and propionate, terpenes such as pine oil, terpineol and the like, solutions of resins such as the polymethacrylates of lower alcohols, solutions of ethyl cellulose in solvents such as pine oil and the monobutyl

5       medium is based on ethyl cellulose resin and a solvent of texanol; alternatively, alpha-beta- and gamma terpineols (generally 85-92% alpha-terpineol containing 8-15% thick film compositions, although poorer burnout properties than the texanol. The medium also may contain volatile liquids to promote fast setting after application to the substrate, thickening and/or stabilizing agents and/or other common additives. The compositions may further comprise additives known in the art, such as colorants and staining agents, rheology modifiers, adhesion enhancers, sintering inhibitors, green-state modifiers, surfactants and the like.

10       The ratio of medium to solids in the dispersions can vary considerably and depends upon the manner in which the dispersion is to be applied and the kind of medium used. Normally to achieve good coverage, the dispersions will contain complementarily 40-60% solids and 60-40% medium and any ranges contained therein.

15       In the preparation of the compositions of the present invention, the particulate solids are mixed with the liquid organic medium and dispersed with suitable equipment, such as a three-roll mill or a power-mixer according to conventional techniques well-known in the art, to form a suspension. The resulting composition has a viscosity generally in the range of about 10-500, preferably in the range of about 10-200, more preferably in the range of about 15-100 Pa.s at a shear rate of 4 sec<sup>-1</sup>, for instance, as measured on a Brookfield RVT viscometer using #14 spindle at 10 rpm and 25°C. The general procedure for preparing the composition of the invention is set out below.

20       The ingredients of the composition are weighed together in a container. The components are then vigorously mixed by a mechanical mixer to form a uniform blend; then the blend is passed through dispersing equipment, such as a three-roll mill, to achieve a good dispersion of particles to produce a paste-like composition having a suitable consistency and rheology for application onto a substrate, for example by screen-printing. A Hegman gauge is used to determine the state of

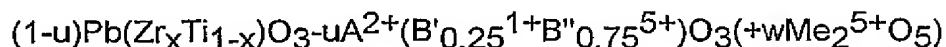
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dispersion of the particles in the composition. This instrument consists of a channel in a block of steel that is 25  $\mu\text{m}$  deep (1 mil) on one end and ramps up to zero depth at the other end. A blade is used to draw down composition along the length of the channel. Scratches appear in the channel where the agglomerates' diameter is greater than the channel depth. A satisfactory dispersion will give a fourth scratch point of typically 10-15  $\mu\text{m}$ . The point at which half of the channel is uncovered with a well-dispersed composition is between 3 and 8  $\mu\text{m}$  typically. Fourth scratch measurements of >20  $\mu\text{m}$  and "half-channel" measurements of >10  $\mu\text{m}$  indicate a poorly dispersed suspension.

- 10 The compositions are then applied as a paste to a substrate, which is a piezoelectrically active material, using conventional techniques known in the art, typically by the process of screen printing, to a wet thickness of about 10-40  $\mu\text{m}$ , preferably about 15-30  $\mu\text{m}$ . The compositions of this invention can be printed onto the substrates either by using an automatic printer or a hand printer in the conventional manner. Preferably, automatic screen printing techniques are employed using a 200- to 400-mesh per inch screen.

A low sintering piezoceramic, according to DE 198 40 488 A1 which is incorporated by reference hereto is used in this invention. The ceramic is disclosed as a lead zirconium titanate piezoelectric ceramic material corresponding to one of the following general formulas:



wherein

$\text{A}^{2+}$  stands for alkaline earth metal ions, preferably for  $\text{Sr}^{2+}$  and/or  $\text{Ba}^{2+}$ ;

$\text{B}'$  stands for alkali metal, preferably for Na and/or K;

$\text{B}''$  and Me for a 5-valent metal from the series Nb, Ta, or Sb, preferably Nb and x, u, and w have the following meaning:

$$x = 0.40 \dots 0.55$$

$$u = 0 \dots 0.10$$

25 Mixed powders with an average grain size of 0.3-10.0 μm d50, preferably 3 μm for Ag and Pt; internal electrodes of this variant show a pronounced lattice-like structure,

Co-precipitated powder with an average grain size of 0.3-3.0 μm d50, preferably 1.0 μm d50; internal electrodes of this variant are smooth and not very perforated.

The following metal powder variants show very positive results:

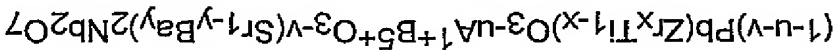
20 to this invention, is described in detail in patents and in the literature.

15 measured electrically. The entire procedure, with the exception of the parts according mesh are soldered onto the base metallization. The actuators are then polarized and means of a screen printing/baking process. The external electrodes of metal wire preferably at 950°C. Subsequently, the base metallization of silver is applied by shaped actuators and these are sintered according to this invention at 875°C-1100°C, stacked and pressed to form a laminate. The laminate is divided into individual, rod-invention is applied to this film by means of screen-printing. Numerous such films are system as a 125 μm thick film. The internal electrode composition according to this The low sintering piezoceramic as identified above is prepared with an organic binder

10  $x = 0.40 \dots 0.55$   
 $u = 0 \dots 0.10$   
 $u, v = 0 \dots 0.05$

5  $A^{1+}$  stands for alkali metal ions, preferably for  $Na^+$  and/or  $K^+$ ;  
 $B^{5+}$ , for a 5-valent metal ion from the series Nb, Ta, or Sb, preferably for Nb;  
 and x, y, u, and v have the following meaning:

wherein



or

(w = 0 ... 1 wt. %)

which forms via partial melting of the silver fraction. The mesh size of the resulting lattice depends on the grain size of the powder being used.

### EXAMPLES

#### Example 1

- 5 A 125  $\mu\text{m}$  green thick film actuator is produced according to the aforementioned procedure.

An interior metallization composition is produced according to the aforementioned procedure. A 90/10 weight percent mixture of Ag and Pt powder is produced as the metallic powder, where the average grain size d50 of each of the two initial powders  
10 is 3.0  $\mu\text{m}$ . The powder is converted to a paste-like composition having a metal content of 47% and a viscosity of 25 Pas with a binder system and a solvent as given below.

| Name   | Wt. %             |
|--|-------------------|
| Tallicin 120 Surfactant                                    | 0.43              |
| N50 Ethyl Cellulose  | 1.25              |
| N200 Ethyl Cellulose                                       | 3.04              |
| Dipentene  | 11.93             |
| Terpineol  | 35.90             |
| Di Butyl Carbitol  | 0.29              |
| Organic Thixotrope   | 0.13              |
| Dehydrated Castor Oil                                      | 0.01              |
| Platinum Powder  | 4.7 s.a. 14-18    |
| Silver Powder  | 42.3 s.a. 0.8-1.4 |
|  |                   |
| Composition Viscosity 20-30 Pa.s<br>(10 rpm Brookfield RVT |                   |
| Grind Gauge <8/3   |                   |

- The above components were mixed as follows:
1. Mix millbase solvents and mediums and surfactants (15-30 min., Hobart mixer).
  2. Mix in metal powders gradually (15-30 min., Hobart mixer).
  3. Wet out (8-16 hours room temperature).
  4. Triple roll mill (usually 3-6 mill passes at increasing pressure until dispersion achieved as indicated by grind gauge).
  5. Make formulation additions medium and solvent to achieve 47% solids and viscosity of 25-35 Pa.s. (10 rpm Brookfield RV7).
- A "green" film is prepared by mixing the ceramic powder according to the above mentioned formula with solvents (e.g. ethanol, butanol), organic binders (e.g. acrylic resins), plasticizers and surfactants. the resulting slurry is casted to a thin film, and dried at a temperature of 80 °C using the "Doctor blade process"(described e.g. in US 5,406,146 or in S. Takahashi et al in Ferroelectrics, 1983, Vol. 90, page 181-190). After drying the green film has a thickness of 125 µm. The formulations of the slurry and the casting process are well known to those skilled in the art.
- After cutting the film into sheets that fit into the following process, the metallisation is printed onto the green ceramic by means of screen-printing, so that, after the drying process, the thickness of the printed layer is 5-8 µm.
- 400 such films are superimposed and pressed at elevated temperature to form a block. The block is separated into individual rod-shaped actuators by means of a cutting tool.
- The actuators are pyrolyzed at 400°C and sintered at 950°C for 10 h. Due to the sintering, the internal electrodes obtain a pronounced lattice-like structure with a mesh size of approx. 6 µm and conductor width of approx. 3 µm. The thickness of the internal electrodes amounts to approx. 3 µm. After sintering, the external dimensions of the actuators amount to 7 x 7 x 40 mm<sup>3</sup>.

External silver electrodes are applied by means of screen-printing and baked at 700°C. A lattice-like wire mesh made of FeNi36 wire as described in EP 0 844 678 A1 with a wire diameter of 75 µm and a mesh width of 175 µm is soldered on for reinforcement. The mesh protects the actuator from electrical  
5 breakdown if cracking of the ceramic or external silver electrodes occurs.

The actuators are then coated by a silicone paint that is state of the art for electronic parts. The coating is hardened at 100°C for 10 hours. Any coating with a sufficient high electrical resistance (  $>10^{12}$  Ohms/cm) can be used here. The polarization occurs at 200 V and 150°C within 2 minutes.

10 Thereafter, on activation with a trapezoid signal with a 100 µs rise/fall time and 1.0 ms hold time at 200 V, the actuators show the following characteristics:

Expansion: 60 µm

Capacitance: 6 µF

Dissipation factor: 40 % (specific for this certain measuring equipment)

15 These values correspond to those of conventional actuators produced with AgPd internal electrodes.

However, in contrast to conventional actuators, no fractures in the actuator occur after continuous stressing with  $10^8$  applied cycles at 160°C.

### Example 2

20 A 125 µm thick green film of SKN53 is produced according to the aforementioned procedure.

An interior metallization composition is produced according to the aforementioned procedure. A 90/10 weight percent mixture of Ag and Pt powder is produced as the metallic powder, where the average grain size d50 of each of the two initial powders  
25 is 3 µm. A PZT powder is added. The powders are converted to a paste-like

composition having a solids content of 47% and a viscosity of 25 Pas with a binder system and a solvent as given below.

| Name                    | Wt. %             |
|-------------------------|-------------------|
| Tallacin 120 Surfactant | 0.43              |
| N50 Ethyl Cellulose     | 1.25              |
| N200 Ethyl Cellulose    | 3.04              |
| DI Butyl Carbitol       | 0.29              |
| Organic Thixotrope      | 0.13              |
| Dehydrated Castor Oil   | 0.01              |
| Ag Powder               | 33.3 s.a. 0.8-1.4 |
| Pt Powder               | 3.7 s.a. 14-18    |
| Dipentene               | 11.93             |
| Terpineol               | 35.90             |
| PZT Powder              | 10                |
| Total                   | 100               |

The components were mixed into a paste-like composition according to Example 1.

5 This composition is printed onto the green film according to Example 1 by means of screen-printing, so that, after the drying process, the thickness of the printed layer is 5-8  $\mu\text{m}$ .

400 such films are superimposed and pressed at elevated temperature to form a block. The block is separated into individual rod-shaped actuators by means of a cutting tool.

10 The actuators are pyrolyzed at 400°C and sintered at 950°C for 10 h. Due to the sintering, the internal electrodes obtain a pronounced lattice-like structure with a mesh size of approx. 6  $\mu\text{m}$  and conductor width of approx. 3  $\mu\text{m}$ . The thickness of the internal electrodes amounts to approx. 3  $\mu\text{m}$ . After sintering, the external dimensions of the actuators amount to 7 x 7 x 40 mm<sup>3</sup>.

External silver electrodes are applied by means of screen-printing and baked at 700°C. A lattice-like wire mesh is soldered on for reinforcement according to Example 1.

5 The actuators are then protected by the said silicone paint coating and the coating is hardened according to Example 1. The polarization occurs at 300 V and 150°C within 2 minutes.

Thereafter, on activation with a trapezoid signal with a 100  $\mu$ s rise/fall time and 1.0 ms hold time at 200 V, the actuators show the following characteristics:

10 Expansion: 63  $\mu$ m  
Capacitance: 6,1  $\mu$ F  
Dissipation factor: 42 % (specific for this certain measuring equipment)  
These values correspond to those of conventional actuators produced with AgPd internal electrodes.  
However, in contrast to conventional actuators, no fractures in the actuator  
15 occur after continuous stressing with  $10^8$  applied cycles at 160°C.

#### Glossary

Tallacin purchased from Pflaumer Brothers Inc.

Thixotrope (MPA2000X) purchased from Rheox Inc.

Ethyl Cellulose purchased from Hercules Inc.

30

in organic medium.  $\sqrt{}$   
metallization comprises finely divided particles of silver and platinum dispersed  
2. Piezoceramic multilayer actuator according to Claim 1, wherein the inner  
and an inner metallization comprising silver and platinum.

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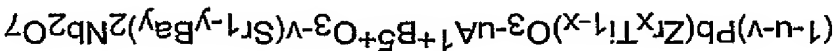
$$\begin{aligned} u, v &= 0 \dots 0.05 \\ u &= 0 \dots 0.10 \\ x &= 0.40 \dots 0.55 \end{aligned}$$

and x, y, u, and v have the following meaning:

20

$B^{5+}$ , for a 5-valent metal ion from the series Nb, Ta, or Sb, preferably for Nb;  
 $A^{1+}$  stands for alkali metal ions, preferably for  $Na^+$  and/or  $K^+$ ;

wherein



15

or

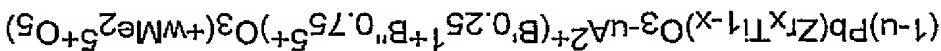
$$\begin{aligned} (w &= 0 \dots 1 \text{ wt. \%}) \\ u &= 0 \dots 0.10 \\ x &= 0.40 \dots 0.55 \end{aligned}$$

and x, u, and w have the following meaning:

10

"B" and Me for a 5-valent metal from the series Nb, Ta, or Sb, preferably Nb  
B' stands for alkali metal, preferably for Na and/or K;  
 $A^{2+}$  stands for alkaline earth metal ions, preferably for  $SR^{2+}$  and/or  $Ba^{2+}$ ;

wherein



5

material being expressed by the following general formulas,

1. A piezoceramic multilayer actuator comprising a low-sintering piezoceramic

What is claimed is:

## CLAIMS



3. Piezoceramic multilayer actuator according to Claim 1, characterized by a sintering temperature of the actuator between 875C and 1000C.
4. Piezoceramic multilayer actuator according to Claim 1, characterized by a sintering temperature of the actuator between 940°C and 960°C.
5. Piezoceramic multilayer actuator according to Claim 1, wherein the particles of the inner metallization composition has a mean grain size d50 of 0.3 µm-10 µm.
6. Piezoceramic multilayer actuator according to Claim 5, characterized by the inner metallization taking on a net-like structure through partial melting during the sintering process.
7. Piezoceramic multilayer actuator according to Claim 1 or 2, wherein the inner metallization further comprises a ceramic powder.
8. Piezoceramic multilayer actuator according to Claim 7 wherein the ceramic powder is a lead zirconate titanate powder.
9. Piezoceramic multilayer actuator according to Claim 7 wherein the ceramic powder is the same composition as the piezoceramic material of the actuator.
10. Piezoceramic multilayer actuator according to Claim 7 characterized by the addition of the ceramic powder having an average grain size in the range of a inner metallization thickness.
11. Piezoceramic multilayer actuator according to Claim 1 or 2 wherein the weight ratio of silver to platinum has a range of 70/30 to 98/2.
12. Piezoceramic multilayer actuator according to Claim 1 or 2 wherein the weight ratio of silver to platinum is 90/10.

- 10 15. Piezoceramic multilayer actuator comprising a low-sintering piezoceramic material e.g. as described in [German patent] DE 198 40 488 A1, characterized by an inner metallization containing silver and platinum.
- 5 14. Piezoceramic multilayer actuator according to Claim 15 wherein the silver and platinum component further comprise ceramic particles.
13. Piezoceramic multilayer actuator according to Claim 2 wherein the inner metallization composition, based on total composition, comprises 40-60 weight % silver and platinum and 60-40 weight % organic medium.

Fig. 1

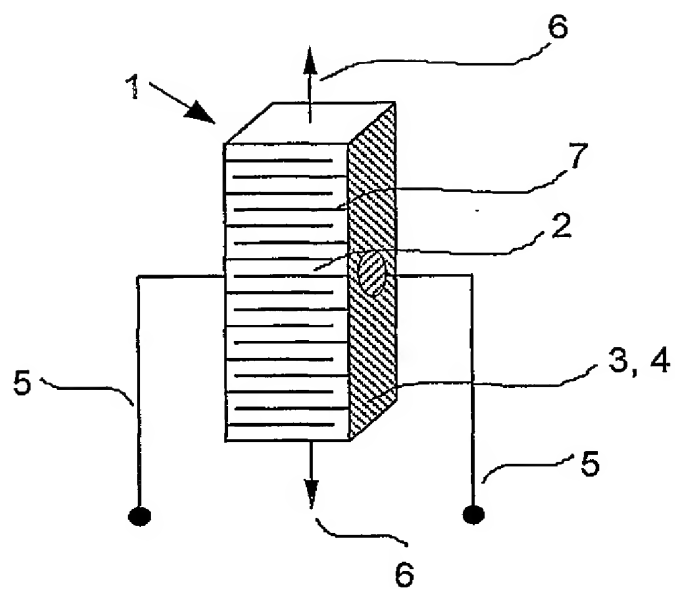
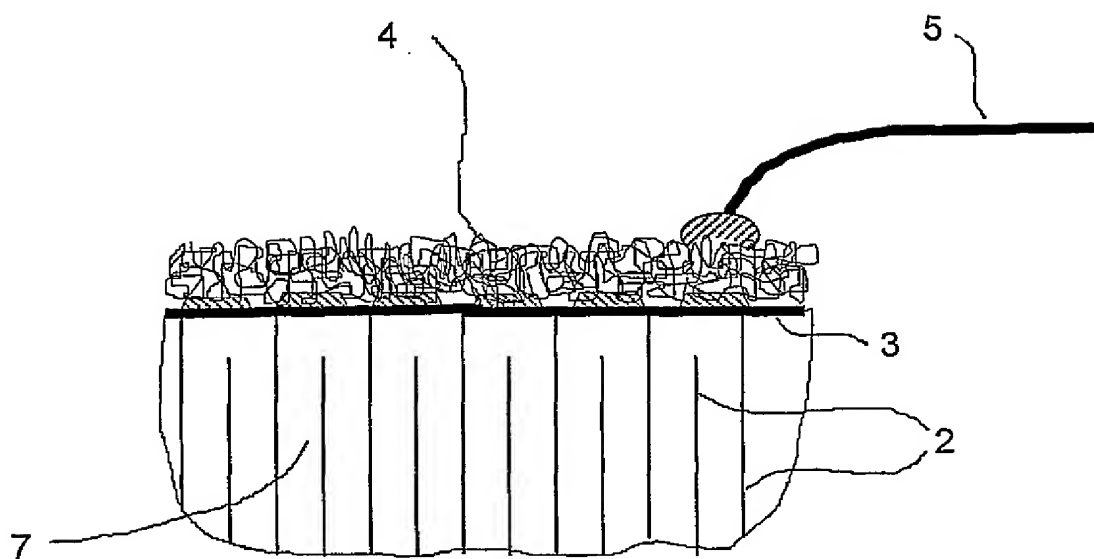


Fig. 2



# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/EP 01/05924

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 7 H01L41/083 H01L41/187 //C04B35/491

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC 7 H01L C04B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)  
EPO-Internal, WPI Data, PAJ, INSPEC

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|----------|--|-----------------------|
|----------|--|-----------------------|

|   |  |                       |
|---|--|-----------------------|
| A | DE 198-40 488 A (CERAMTEC-AG),<br>11 March 1999 (1999-03-11)<br>cited in the application<br>page 3, line 3 -page 6, line 22  | 1, 15                 |
| A | PATENT ABSTRACTS OF JAPAN<br>vol. 1998, no. 02,<br>30 January 1998 (1998-01-30)<br>8 JP 09 261978 A (NIPPON CEMENT CO LTD;<br>CANON INC), 3 October 1997 (1997-10-03)<br>abstract<br>-8 US 6 114 798 A (MARUYAMA YUTAKA ET AL)<br>5 September 2000 (2000-09-05)<br>column 1, line 6 -column 6, line 32 | 1, 2, 5, 7,<br>10, 11 |
| A | WO 92 17420 A (AMERICAN SUPERCONDUCTOR<br>CORP) 15 October 1992 (1992-10-15)<br>page 4 -page 13; examples 3-6  | 1                     |

☐ Further documents are listed in the continuation of box C.  
☒ Patent family members are listed in annex.

## \* Special categories of cited documents:

- \* A\* document defining the general state of the art which is not considered to be of particular relevance
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| Date of the actual completion of the international search | 23 October 2001 |
| Date of mailing of the international search report        | 30/10/2001      |

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| Name and mailing address of the ISA<br>European Patent Office, P.B. 5018 Patentlaan 2<br>NL - 2280 HV Rijswijk<br>Tel. (+31-70) 340-2040, Tx. 31 651 epo nl.<br>Fax: (+31-70) 340-3016 | Köpf, C<br>- Authorized officer |
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**INTERNATIONAL SEARCH REPORT**  
 information on patent family members

International Application No  
 PCT/EP 01/05924

| Patent document<br>cited in search report |   | Publication<br>date | Patent family<br>member(s) | Publication<br>date |
|---|---|---------------------|----------------------------|---------------------|
| DE 19840488                               | A | 11-03-1999          | DE 19840488 A1             | 11-03-1999          |
|   |   |                     | BR 9812150 A               | 18-07-2000          |
|   |   |                     | CN 1269773 T               | 11-10-2000          |
|   |   |                     | WO 9912865 A1              | 18-03-1999          |
|   |   |                     | EP 1025061 A1              | 09-08-2000          |
| JP 09261978                               | A | 03-10-1997          | US 6114798 A               | 05-09-2000          |
| WO 9217420                                | A | 15-10-1992          | EP 0705228 A1              | 10-04-1996          |
|   |   |                     | JP 6506184 T               | 14-07-1994          |
|   |   |                     | WO 9217420 A1              | 15-10-1992          |
|   |   |                     | US 5318725 A               | 07-06-1994          |

